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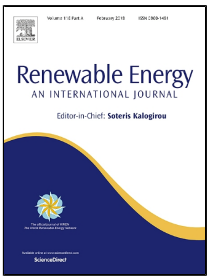

Coupled effect of torrefaction and blending on chemical and energy properties for combustion of major open burned agriculture residues in Thailand

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Highlights

- Torrefaction at high temperature of agriculture residues blends has been investigated
- Energy density increasing and chlorine content mitigation has been observed for torrefied biomass
- Positive and/or negative synergistic effects were observed during co-pyrolysis of the mixtures.
- Ignition and burnout temperature have been calculated for raw and torrefied biomass

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Coupled effect of torrefaction and blending on chemical and energy properties for combustion of major open burned agriculture residues in Thailand

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Abstract

Thailand is an agriculture-based country. It produces large amounts of open burned agricultural residues. A strategy to use them as biofuel all year round is to enhance their fuel properties by coupling blending and thermochemical pre-treatment. In this study, the pyrolytic behaviour of major residues (napier grass , rice straw, cassava stalks and corn cob) exposed to a high torrefaction temperature (300°C) was investigated for various blending ratios, i.e. 100:0, 50:50 and 70:30. The release of chlorine was quantified for each biomass blend, including, a new fouling risk index ratio. Also, the synergistic effects of both ignition and burnout temperatures were analysed. Rice starw and napier grass were found to be characterised by a high ash content and so large amounts of solid yield after torrefaction. Raw biomasses and untreated biomass blends were found to be less suitable as biofuel than torrefied biomasses. The ratio K2O:SiO2, indicator of fouling risk during combustion, was found to be low for all torrefied blends. The HHV:Cl ratio, indicator of combustion quality, indicated that NG mixed with RS (50:50 proportion) is the most promising blend. Significant synergetic effects were observed for biomasses mixed before torrefaction. The burnout temperatures for raw and torrefied biomasses were identified in the range 773-787 °C and 786-795 °C.

Keywords: Torrefaction; Crops; Blends; Chlorine; Synergetic effect; Ignition and burnout temperatures.

1. Introduction

Thailand is an agriculture country rich in biomass resources. This sector has played a significant role in terms of economic contribution since historical times. From a total area of 0.5 million square kilometres, more than 65% is subject to agricultural activities. With the ever increasing market demand for agricultural products, most of the agricultural residues generated in the country end up in municipal waste streams or in other cases are not efficiently used (Visvanathan *et al.* 2008, Tangwanichagapon *et al.* 2017) There are more than ten millions tons of agriculture waste and residues generated per year. To simultaneously solve the dilemma of energy demand (from 75 Mtoe in 2014 to 131Mtoe by 2036), waste management and greenhouse gas emissions (Cop 21 commitments), the Thai Ministry of Energy has set up an Alternative Energy Development Plan aiming at increasing alternative energy consumption from 10 Mtoe in 2014 to 40 Mtoe by within 20 years. The plan's target is to increase the use of biomass for renewable energy to 5.5 MW by 2036, while the generating capacity of 2014 was 2.5MW (Tantiwatthanaphanich *et al.* 2016). High potential of agricultural waste

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can be utilized for factories and biomass power plants. However, the industry is still facing challenges to manage these wastes because of their limitations as fuel, including: 1) not available throughout the year, 2) low bulk density leading to high transportation costs, 3) low heating value coupled with high moisture content, 4) strong heterogeneity requiring therefore pre-treatment and 5) ash content higher than woody biomass with high chlorine content resulting in operational problems including deposit formation and boiler corrosion during combustion (Kassman *et al.* 2013). For all these reasons, factories and power plants using biomass tend to reduce or stop operation replacing it by fossil fuels.

One of the strategies to enhance fuel properties of agricultural waste and limit deposition, slagging, fouling and corrosion in thermal fuel conversion systems is to apply torrefaction (Starfelt *et al.* 2015). Torrefaction, as a moderate thermal treatment at temperatures ranging from ~200 to 300°C in an inert atmosphere (Bach *et al.*), transforms biomass properties close to those of fossil coal. Torrefaction is used to produce a fuel with increased energy density and improved grindability, thereby reducing costs of transportation, milling and storage. The reader will find more details in this complete critical literature review (Chen *et al.* 2015).

Another significant observation is that torrefaction reduces the chlorine content of biomass. The release of chlorine during combustion of biomass has been investigated in a number of publications (Knudsen *et al.* 2004, Johansen *et al.* 2013). Few studies have measured the fate of ash-forming elements, including chlorine at temperatures relevant to torrefaction. Saleh and co-authors (Saleh *et al.* 2014) investigated the release of chlorine from different biomasses in the temperature range of 150-500°C. Results showed that the release of chlorine from wheat straw was first observed at 250 °C (20%) and peaked with about 60−70% at 350 °C. For woody biomass, most of the chlorine would be released at 350 °C. Keipi (Keipi *et al.* 2014) observed a very high reduction in chlorine content (90%) with Eucalyptus wood heated at 260°C during 60min. Contrary to these results, other studies showed that less than 10% of chlorine would be evaporated from the fuel at 200°C and only 20 to 50% at 400 °C (Björkman *et al.* 1997). A recent study using thermodynamic equilibrium calculations to better understand the release mechanism of chlorine during agricultural waste pyrolysis concluded that the evaporating process can be divided into two temperature ranges: a fast evaporating process from 200 to 600°C and a slow evaporating process from 600 to 1000°C (Toptas *et al.* 2015). These results corroborate the one obtained by Jensen (Jensen *et al.* 2000) where 60% of chlorine was released when the temperature increased from 200 to 400°C and most of the residual chlorine was released between 700 and 900°C. Most of the studies concluded that the release ratio of chlorine increased continuously with temperature and holding time and is linearly proportional to devolatilization. Other parameters can play a role during mild pyrolysis. The particle size and sample weight are also important factors influencing chlorine release mainly due to the secondary reactions. A recent study showed that the release ratio for 74–124μm straw particle was 60.78%, which was much higher than 27.25% for 250–420μm at 350 °C (Chen *et al.* 2016). The changes in the chemical association of ash-forming elements are also different for the four macromolecules (cellulose, lignin, xylan and pectin). These results provide new data about chemical changes with regards to the inorganic elements during torrefaction (Thanarak 2012).

The advantages of torrefaction are particularly recognized for use in older and existing pulverized coal-fired power plants because it provides a technical option for high substitution ratios of biomass. The direct co-combustion plants operate generally with a blend containing a maximum of 5 to 10% biomass. New coal-fired power plants are designed for high co-firing ratios of lignocellulosic biomass, much more than 40% with torrefied biomass without decreasing of energy efficiency and fluctuation of boiler load (Li *et al.* 2012). The reactivity of blend containing lignocellulosic biomasses was found similar to that of lignite (Toptas, Yildirim et al. 2015). It is clear that using torrefied agricultural residues and their blends is a very effective and sustainable innovative way to dispose waste materials throughout the year. Many studies have focused on improved physicochemical properties of torrefied woody biomass but few on blends of agriculture crops.

The first objective of this study is to investigate the torrefaction at high temperature (300°C) of four agricultural residues widely available in Thailand via non-isothermal thermogravimetric method. Also the additive behaviour according to the blend ratios will be discussed to predict the optimized mixture

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for a better used during the whole year. The second objective is to quantify at a macroparticule scale the release of chlorine from individual and blended biomasses exposed to the same torrefaction conditions, operating in a batch reactor under nitrogen.

2. Methodology

2.1. Samples

The four biomasses, including rice straw, napier grass, corn cob and cassava stalks that were used in this study represent major crops in Thailand and were collected in Nakhon Ratchasima province, in the North East region. These abundant agricultural materials are traditional energy feedstocks used in rural areas and the industry (Tantiwatthanaphanich and Zou 2016). Prior to the experiments, all the samples were dried and ground by a cutting mill, and sieved to a particle size of around 0.5–2 mm for the torrefaction test in the furnace and 0.1mm for the thermogravimetric study with TG. The biomass blends were prepared by physical mixing grinded biomass in the proportion of 50:50 and 70:30 before and after torrefaction. Because napier grass has the highest chlorine content, this study focused on blending this biomass material with the three other residues successively.

2.2. Torrefaction

Experiments were conducted in a horizontal quartz tube reactor and a thermogravimetric analyser **(Figure 1).** About 1.5–2.5 g of sample was placed in an alumina boat located in the middle of the quartz reactor. Nitrogen was then purged through the reactor at a flow rate of 100 ml/min. Then the reactor was heated to the desired temperature (300°C) at a heating rate of 10°C/min which is maximum rate reached for mostly all industrial reactors and held at the desired time (5 minutes). After cooling down to room temperature, the solid product was weighed to measure the mass and energy yield which is defined as fuel value of solid product as a fraction of fuel. Energy yield indicates the magnitude of energy conversion of the initial biomass after torrefaction, while the mass product yield represents the mass conversion. The energy density of torrefied solid products represents the ratio between the increased energy yield and the converted mass yield. The pyrolysis thermal behaviour of both samples (about 5-6 mg biomass per run) and their blends were investigated using a thermogravimetric analyser TG (Perkin-Elmer, pyris1). The synergistic effects have been reported by many researchers, for co-pyrolysis (Lu *et al.* 2013) or co-combustion (Goldfarb *et al.* 2013, Sarkar *et al.* 2014). If there are no interactions in the thermal decomposition of the four biomasses, the pyrolysis characteristics of the blends will follow the behaviours of their parent materials in an additive manner. To evaluate the interactions between the different raw and torrefied biomasses, the calculated TGA thermograms were compared to the ones obtained via the experiments. The equation below was used (Toptas, Yildirim et al. 2015).

$$\mathrm{Bsum}(dm/dt)_{sum} = B_1\,(dm/dt) + B_2\,(dm/dt)$$

Where, B_1 is the mass fraction of biomass 1 in the blend, $B_2 = 1\text{-}B_1$ is the mass fraction of biomass 2 in the blend, (dm/dt) is the weight loss rate ($g.min^{-1}$).

If overlapping is observed between experimental and calculated curves, it means blend pyrolysis characteristics present an additive behaviour, or, in other words, no synergistic effects between the components of the blends are observed.

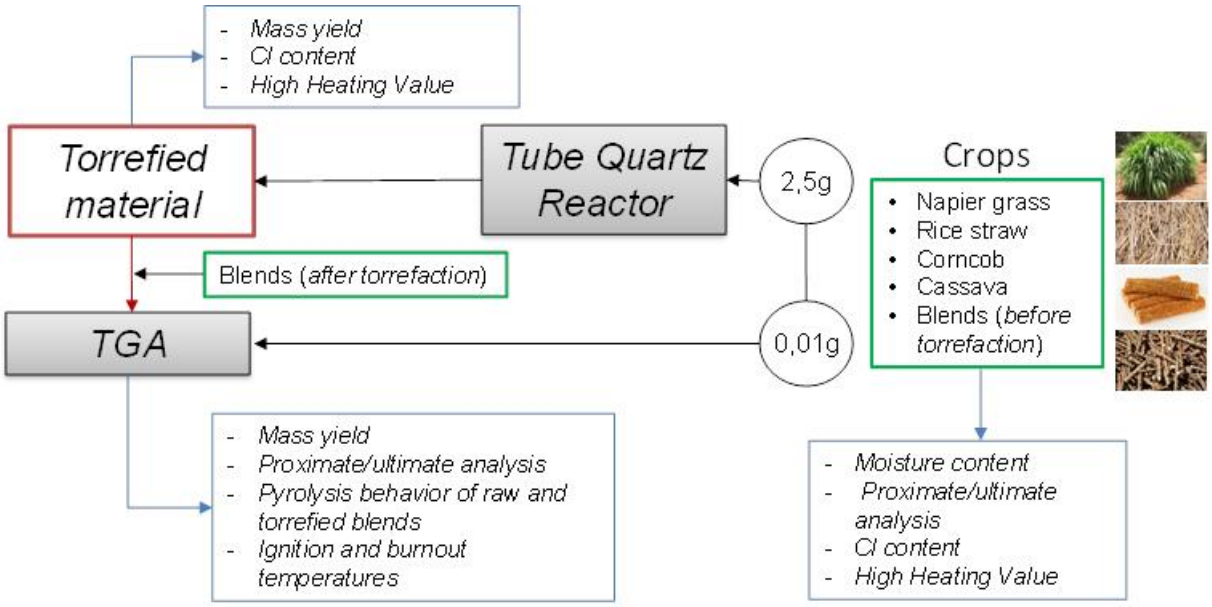

Figure 1 : Schematic diagram of experimental set-up of torrefaction in horizontal quartz tube reactor and TGA.

The proximate analyses of the pre-treated materials followed the standard procedure of the American Society for Testing and Materials (ASTM D5142). The heating program was as follows: hold 10 min at 110°C (drying phase), ramp up to 900°C at a heating rate of 10°C/min, and finally hold 10 min at 900°C with air at a flowrate of 50mL/min. The elemental analysis was analysed by use of an elemental analyser (Thermo FlashEA 1112). A number of equations have been published that relate the elemental composition to the higher heating value (HHV) of coal, biomass and municipal waste (Friedl *et al.* 2005). Dulong's formula was selected in this study for estimating the heating value on the basis of the elemental composition of biomass (Hosokai *et al.* 2016). Assessment of chlorine content was performed by X-ray fluorescence (XRF) spectrometry, a rapid method used to determine the composition of biomass ash (Xing *et al.* 2016). As recommended by a recent study comparing different methods to calculate the ignition (Ti) and burnout temperatures (Tb), we adopted the intersection method (IM) and the conversion method (CM) to obtain accurate Ti and Tb, respectively (Lu *et al.* 2015).

3. Results

Three different biomass blending ratios were taken into consideration: 100:0, 50:50 and 70:30%. When the ratio is equal to 100%, it means that raw biomass alone was tested. The notification of biomass is: NG = Napier grass; RS = Rice straw; Ca = cassava stalks and Co = Corn cob. The blends are denoted "NG70RS30" where NG and RS were the biomass, and 70 and 30 the respective ratios in %. Also, "Raw" and "Tor." denotes untreated and torrefied biomass respectively.

3.1. Properties of raw and blended biomass

The physical and chemical properties of raw and blended biomasses (untreated and torrefied) are presented in **Table 1Error! Reference source not found.**. As mentioned in the literature, it is well-known that torrefaction increases fixed carbon content and reduces volatiles content. RS and NG showed the highest ash content while Ca and Co the lowest. As expected, fixed carbon increased with the torrefaction for all raw and blended biomasses. Since the volatile matter components mainly react under high temperatures over 200 °C, the amount can affect the changes of torrefied solid mass and energy. On the other hand, FC and ash are the main components of the remaining solid products after the release of the volatile matters, which contribute to large amounts of solid yield after the torrefaction process.

The relative proportion of fixed carbon (FC) and volatile matter (VM), called fuel ratio (Du *et al.* 2014), is a method originally designed for the characterization of coal. After torrefaction, the FC:VM ratio may significantly change. It was found that torrefaction is more efficient for RS followed by Ca, Co and NG with 0.51, 0.46, 0.44 and 0.36 respectively. All torrefied mix with a 50:50 ratio presented similar values around 0.4 while 70:30 ratios exhibited stronger differences, ranging from 0.3 up to 0.7. Clear relationships between FC:VM and lignin:cellulose content in biomass samples are likely confounded by the presence of minerals, some of which exert a strong influence on the yields and qualities of thermochemical conversion products due to catalytic activity (Tanger *et al.* 2013). According to the energy density, RS had the lowest enhancement factor (1.26) among the four species, as a result of a high ash content. If considering the lowest ash content and the highest HHV as indicators of combustion quality, the best blends were NG50Co50 and NG50RS50.

The elemental composition of the bio-char produced from each blend did not reflect the ratio of the individual biomass types. As shown in **Table 1 Error! Reference source not found.**, the mean elemental composition of the four feedstock types did not match the composition of the corresponding blends. This result indicates that different reactions and interactions occurred during the torrefaction of each feedstock and of each blend for the same conditions, which led to a different elemental composition for the biochar produced from each blend. It is well known that a higher proportion of hydrogen and oxygen reduces the energy value of biomass fuel compared to fossil fuel. The significance of the O:C and H:C ratios on the CV of solid fuels can be illustrated using a van Krevelen diagram (**Figure 2**). The premise in this classification is that biomass feedstocks that fall within clusters will have similar properties, regardless of their category. From the results obtained, it observed that the biomass feedstocks can be broadly classified into four groups based on the general assessment of their source. Raw and blended untreated biomasses showed lower aptitude as biofuel than torrefied biomass. Compared to the average 35% oxygen content of torrefied biomass in dry-ash-free condition, raw biomass has higher oxygen content (around 50%). Therefore raw biomass is expected to produce more oxygenated volatile compounds than torrefied biomass. The torrefied biomass blends displayed the lowest dispersion. Change in elementary composition of the torrefied blends leads to a shift toward the origin of the graph. This can be attributed to the catalytic effect of inorganic matter, catalysing the pyrolysis reactions leading to the formation of more energetic biofuel. In the same time, the liberated compounds contain higher proportions of oxygen and hydrogen than carbon, thus reducing the relative concentration of these elements in the solid residue. The H:C and O:C molar ratios of NG50Co50 were found to be 1.1 and 0.54. These are higher than the values obtained for NG70Co30 (H:C 1.3 and O:C 0.48).

Other parameters such as volatile matter or fixed carbon do not correlate as well, because these parameters are strongly influenced by both heating rate and ash content/composition. It is noted that the fuel ratio of torrefied blends (FC:VM) was < 2.5, which shows that satisfactory combustion performance can be obtained from all biomass feedstocks blended in pulverized fuel firing system (Sarkar, Sahu et al. 2014).

Table 1: Properties of raw and torrefied blends. EF = Enhancement Factor which is the ratio HHV torrefied biomass/HHVraw biomass

Materials		*Proximate analysis (wt%, d.a.f.)*					*Ultimate analysis (wt%, d.a.f.)*			
		Volatile matter	Ash	Fixed Carbon	***FC:VM***	EF	C	H	N	O
Napier grass	Raw	78.8	11.2	10.0	***0.13***	1.43	41.00	5.99	1.43	51.57
(NG)	Tor.	62.0	15.5	22.3	***0.36***		56.42	7.19	1.62	34.77
Rice straw	Raw	75.9	11.8	12.3	***0.16***	1.26	41.38	7.10	1.47	50.05
(RS)	Tor.	56.0	15.7	28.3	***0.51***		52.08	7.21	0.86	39.84
Cassava stalks	Raw	81.3	7.0	11.7	***0.14***	1.66	36.88	6.75	1.47	54.89
(Ca)	Tor.	61.6	10.2	28.2	***0.46***		57.15	8.64	1.88	32.32
Corn cob	Raw	86.3	3.7	10.0	***0.12***	1.54	39.88	6.62	1.68	51.83

(Co)	Tor.	65.7	5.6	28.7	***0.44***		56.73	9.10	1.38	32.79
NG50RS50	Raw	76.0	11.5	13.0	***0.17***	1.71	42.00	6.00	1.00	51.00
	Tor.	52.0	25.0	23.0	***0.44***		64.00	8.00	2.00	26.00
NG70RS30	Raw	78.0	11.4	11.0	***0.14***	1.64	41.00	6.00	1.00	51.00
	Tor.	58.0	22.0	20.0	***0.34***		62.00	8.00	2.00	28.00
NG50Ca50	Raw	79.0	9.1	12.0	***0.16***	1.68	39.00	5.00	2.00	54.00
	Tor.	58.0	16.0	25.0	***0.43***		61.00	8.00	2.00	29.00
NG70Ca30	Raw	77.0	9.9	13.0	***0.16***	1.67	41.00	6.00	2.00	51.00
	Tor.	58.0	18.0	24.0	***0.42***		63.00	8.00	3.00	26.00
NG50Co50	Raw	83.0	7.5	9.0	***0.11***	1.47	42.00	6.00	2.00	59.00
	Tor.	57.0	15.0	28.0	***0.48***		59.00	7.00	2.00	32.00
NG70Co30	Raw	79.0	8.9	10.0	***0.13***	1.57	42.00	6.00	2.00	50.00
	Tor.	50.0	15.0	35.0	***0.71***		60.00	8.00	2.00	29.00

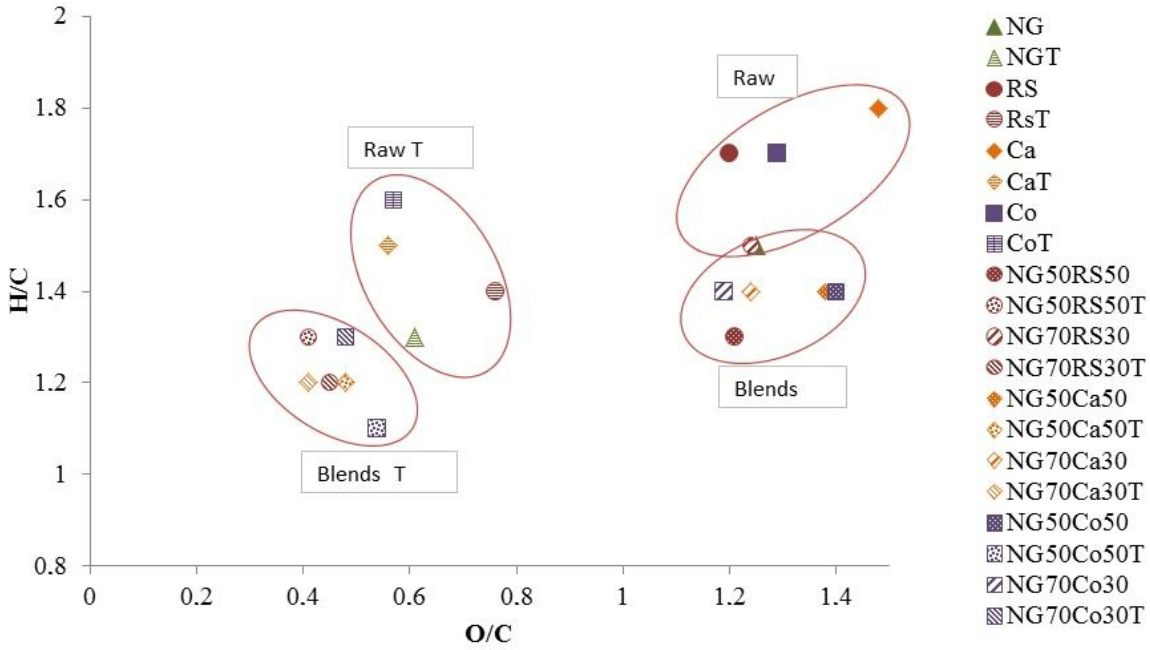

Figure 2: Van Krevelen plot of H/C against O/C for all raw and blended biomasses. T = torrefied.

3.2. Fouling risk index and chlorine release

For the utilization of biomass as energy feedstock, ash composition is a critical parameter. A considerable amount of information is available about these species (Mäkelä *et al.* 2016). Many biomass fuels lead to slagging and fouling in the boiler.**Error! Reference source not found. Table 2** gives an overview of properties of biomass ashes with a special emphasis on their erosion and corrosion potential. A fouling risk ratio K_2O/SiO_2 was adapted based on information from the literature to determine which biofuel requires special precautions to avoid fouling problems (Hustad *et al.* 2000). Lower this ratio, more precautions must be taken to avoid erosion which can occur from higher silica content. All torrefied blends were found to have lower K_2O/SiO_2 ratio than untreated ones. This is mainly due to the increase in inorganic elements after torrefaction. NG blended with RS

at a 50:50 ratio presented the lowest combustion properties (0.6). However, NG blended with Ca in the same proportion showed the most promising combustion properties (1.4). This can be explained by the low silica content of cassava stalks. When increasing the blending ratio to 70:30, the fuel ratio decreased due to the ash composition of NG which is richer in SiO_2. A dilution phenomenon of inorganics was therefore observed when mixing biomasses.

Straw typically contains large amounts of chlorine. The chlorine content of torrefied biomass was measured and compared to that of original fuel. **Figure 3** shows the evolution of heating value versus chlorine content for all raw and blended biomasses torrefied at 300°C. It was observed that there were no significant differences in HHV between the biochars produced from the different biomass feedstocks as well as no significant differences between the individual feedstocks and corresponding blends. All raw and blended untreated biomasses presented similar heating values at around 16 $MJ.kg^{-1}$ whichever the blending ratio applied. This can be explained by the elemental composition of the parent biomasses which are roughly similar. These observations indicate that torrefaction temperature and feedstock type do not significantly affect biochar elemental composition, MC, and HHV corroborated by a recent study (L. Wei *et al.* 2017). One observed cassava was the most sensible to the heat treatment increasing the HHV up to $25MJ.kg^{-1}$ while RS presented the lower value ($21\ MJ.kg^{-1}$) validating the EF values calculated in **Error! Reference source not found.**. After torrefaction, HHV was found to range from 24 to 28 $MJ.kg^{-1}$ for all blends. The maximum was for NG and RS (50:50). Since HHV is a mass based measurement, high mineral content leads to a decrease in HHV, because minerals contribute little energy during biomass oxidation.

Table 2: Ash analysis of raw and blended biomasses. d.a.f = dry ash free. Tor. = torrefied.

		Chemical analysis (wt%, d.a.f)							
Material		SiO_2	K_2O	***K_2O:SiO_2***	CaO	P_2O_5	MgO	SO_3	Fe_2O_3
NG50RS50	Tor.	49.8	29.2	***0.6***	9.0	2.3	1.5	1.2	0.7
NG70RS30	Tor.	43.6	32.0	***0.7***	10.1	2.7	2.1	1.2	1.0
NG70Co30	Tor.	29.5	34.8	***1.2***	18.3	4.2	2.6	1.7	1.4
NG70Ca30	Tor.	31.5	38.5	***1.2***	12.2	3.5	2.3	1.5	2.1
NG50Co50	Tor.	30.7	39.3	***1.3***	12.2	3.6	2.1	1.6	2.5
Rice straw (RS)	Raw	27.6	38.6	***1.4***	17.4	1.8	0.2	0.8	2.3
Rice straw (RS)	Tor.	28.8	41.0	***1.4***	16.2	1.7	0.2	0.5	1.9
NG50Ca50	Tor.	24.4	35.2	***1.4***	22.6	5.1	2.7	1.9	1.5
NG50RS50	Raw	19.3	44.4	***2.3***	18.4	2.0	0.3	0.9	1.8
NG70RS30	Raw	15.9	46.7	***2.9***	18.7	2.0	0.3	1.0	1.6
Napier grass (NG)	Tor.	11.9	51.3	***4.3***	18.8	1.9	0.4	0.7	1.1
Napier grass (NG)	Raw	10.9	50.2	***4.6***	19.3	2.2	0.4	1.1	1.3
NG70Co30	Raw	10.2	47.6	***4.7***	16.3	2.8	0.3	1.2	8.3
NG50Co50	Raw	9.7	45.8	***4.7***	14.3	3.3	0.3	1.4	13.0
Corn (Co)	Raw	8.5	41.4	***4.9***	9.3	4.4	0.3	1.6	24.8
NG70Ca30	Raw	8.9	44.7	***5.0***	27.4	2.6	0.4	1.2	2.4
Corn (Co)	Tor.	10.0	52.2	***5.2***	10.0	3.7	0.4	0.9	16.0
NG50Ca50	Raw	7.6	40.9	***5.4***	32.9	3.0	0.4	1.3	3.2
Cassava (Ca)	Raw	4.2	31.7	***7.6***	46.5	3.7	0.4	1.4	5.0
Cassava (Ca)	Tor.	3.0	36.8	***12.2***	46.6	3.4	0.4	0.9	3.8

All biomass groups showed a similar trend with a decreasing content in chlorine. From the perspective of different biomass types (raw and blended), the amount of chlorine compounds varied from 3.3 to 13.5% before torrefaction and from 1.6 to 12.5% after torrefaction. A slight decrease was observed for

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NG while the 3 other biomasses showed a more emphasised mitigation in chlorine concentration. With respect to the releasing mechanism, at lower temperatures, the release of Cl was mainly caused by the following reaction: $2KCl + nSiO_2 + H_2O \Rightarrow K_2O(SiO_2)n + 2HCl$, as KCl and SiO_2 in biomass inorganic matters react with water contained in biomass and result in the formation of silicate and HCl (Du, Wang et al. 2014). At 300°C, approximatively 7 to 60% and 35 to 56% of chlorine were released from the raw and blended biomasses respectively. These results are consistent with earlier findings concluding that approximatively 70% of chlorine is released at 350°C with no further release at 500°C (Saleh, Flensborg et al. 2014). The literature reports that during this phase called fast evaporating range, 60% of chlorine is evaporated in the gas phase predominately as HCl and 40% is released in the liquid phase at 300°C. Therefore, the combustion of torrefied biomass containing less chlorine than raw biomass generates significantly lower HCl emissions than raw biomass, particularly so for biomass of low alkali content (Ren *et al.* 2017). In terms of combustion, torrefied Ca is the most advantageous biofuel as characterised by the highest heating value (25 $MJ.kg^{-1}$) coupled with the lowest amount of chlorine (1.6%) contributing thereby to minimising slagging and fouling issues. A HHV:Cl ratio was therefore established in this work to provide information about the quality of various biomass blends as biofuel and also some qualitative insights about biomass combustion. The higher the ratio, the better the combustion properties. As shown previously, NG mixed with Ca (NG50Ca50) was expected to be the most promising biofuel (with a ratio of 5.7). However, when NG was blended with RS (NG50RS50), a higher ratio was obtained (6.3). NG70Co30 was found to have a lower ratio (3.9). These results allow us to conclude that the mixing and torrefaction of two biomasses with high chlorine content and low energy density contribute to improve significantly the combustion properties of the blend.

The transformation property of chlorine during biomass torrefaction as a percentage reduction of the original content is shown in **Table 3Error! Reference source not found.**. This value is associated with solid yield and energy yield as these three parameters are the main indicators of the torrefaction quality. For all biomasses, the energy yield was found to be higher than the solid yield. The yields of torrefied biomass were found to be almost similar ranging from 56 to 59% and 53 to 57% for raw and blend respectively. Torrefied cassava showed the highest energy yield with 95% and half of chlorine was released when RS showed the lowest energy (76%) and lowest chlorine reduction (18%). According to these, NG blended with Ca (50:50) was the least reactive to temperature and presented the highest solid and energy yield with 56.7 and 95.3% respectively while chlorine content was reduced by 44%. The greatest reduction in chlorine content was observed for the blend NG50RS50 with 56%.

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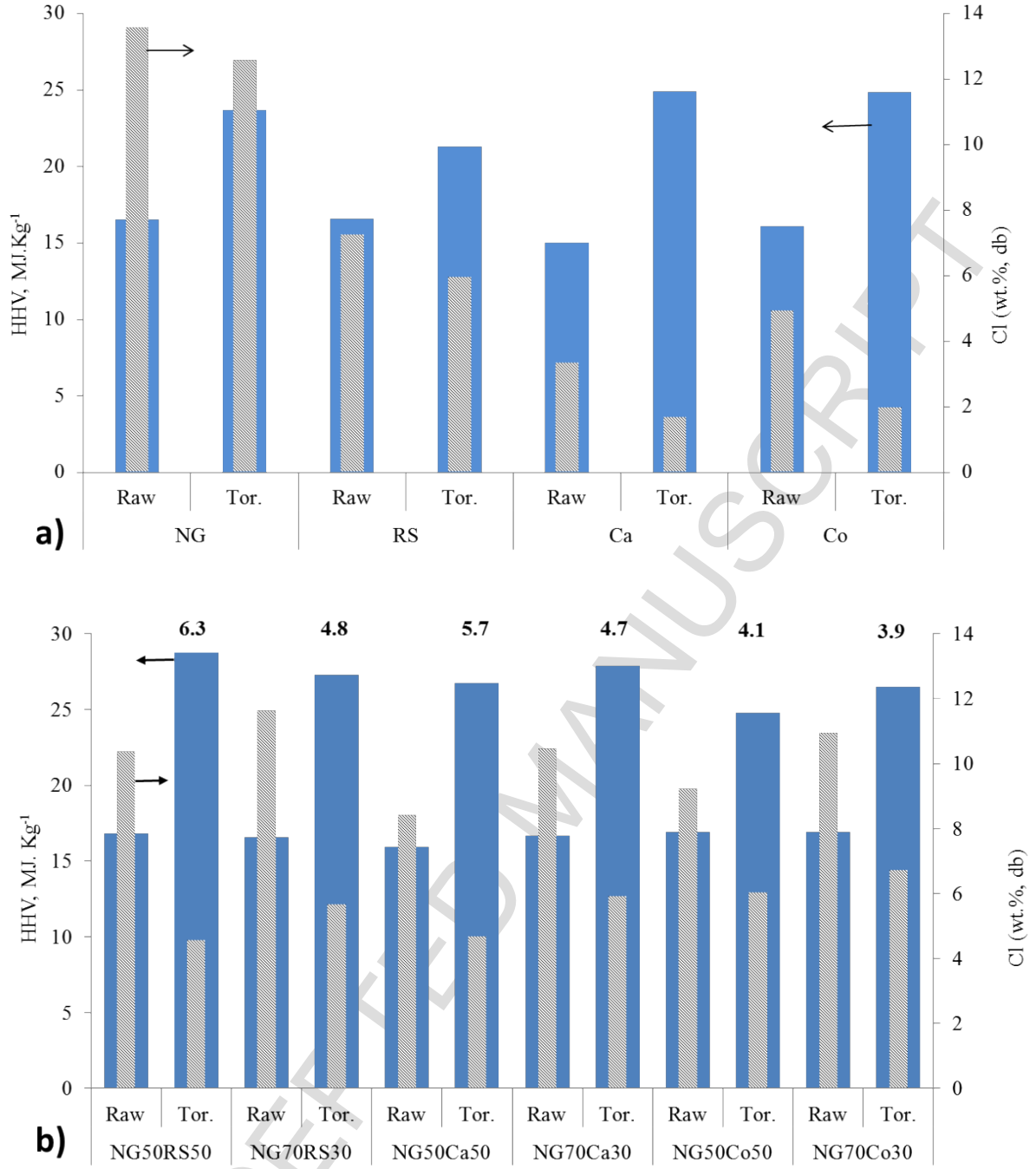

Figure 3: a) HHV vs Cl content for all biomasses before (Raw) and after torrefaction (Tor.) at 300°C. 5min. b) HHV vs Cl content for all blends before (raw) and after torrefaction (Tor.) at 300°C/5min. The calculated HHV/Cl values are shown in bold. NG=Napier grass; RS = Rice straw; Ca = Cassava stalks; Co = Corn cob.

Table 3: Mass (M) and energy (E) yield and chlorine reduction (red.) of torrefied biomasses and torrefied blends.

	NP	RS	Ca	Co	NG50RS50	NG70RS30	NG50Ca50	NG70Ca30	NG50Co50	NG70Co30
M. yield (wt.%)	55.6	59.2	57.6	56.8	53.8	53.9	56.7	52.8	53.6	54.1
E. yield	79.7	76.0	95.4	87.6	91.9	88.6	95.3	88.2	78.7	84.9

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(%)										
Cl red. (%)	7	18	50	60	56	51	44	43	35	39

3.3. Pyrolysis behaviour of individual and blended biomasses

The pyrolysis of lignocellulosic materials plays an important role as first chemical step in the combustion process as a large part of the original biomass is converted to volatile products . The behaviour of individual biomasses and torrefied biomasses in nitrogen atmosphere was investigated and the results displayed in **Figure 4**. According to the distributions of TGA curves, two groups composed of raw and torrefied biomasses can be observed. Torrefied biomasses were found to be less reactive than the control. At 800°C, the solid residues of raw RS, NG, Ca and Co were found to amount to 30, 29, 27 and 20% respectively, while for torrefied RS, Ca, NG and Co, they amount to 46, 41, 40 and 30% respectively. A significant weight loss for raw and torrefied Co was observed above 300°C unlike the three other feedstocks investigated. This is because Co contains more holocellulose. Other torrefaction studies reached similar conclusions.

The DTG curve for NG was plotted only assuming that all fuels were characterized by the same four-stage thermal degradation as shown by Lu and his co-authors (Lu, Lee et al. 2013). The decomposition of the fuel mainly took place in the second stage. The decomposition intensity of untreated NG (0.8 $wt\%°C^{-1}$) was found to be significantly higher than the torrefied one (0.5 $wt\%°C^{-1}$). It was also observed that during the torrefaction process at temperatures above 275°C (in addition to moisture removal), the lignocellulosic structure of the biomass was partly thermally degraded. This concerned especially the reactive hemicellulosic fraction. The degradation of this component during heating significantly reduces the amount of free reactive hydroxyl groups, which causes relatively more cellulose and lignin to be contained in the torrefied biomass, leading to its lower reactivity. As confirmed by a previous study, in addition to the thermal degradation of cellulose at temperatures above 300°C, the 3rd stage starting at 430°C corresponds to a mild decomposition process attributed to the reaction of lignin (Chen, Peng et al. 2015). It can be observed, as expected, that the decomposition of raw and torrefied biomass was approximatively similar. The last stage corresponds to carbon element enrichment with hydrogen and oxygen volatilized as shown in the van Krevelen diagram (**Figure 2)**.

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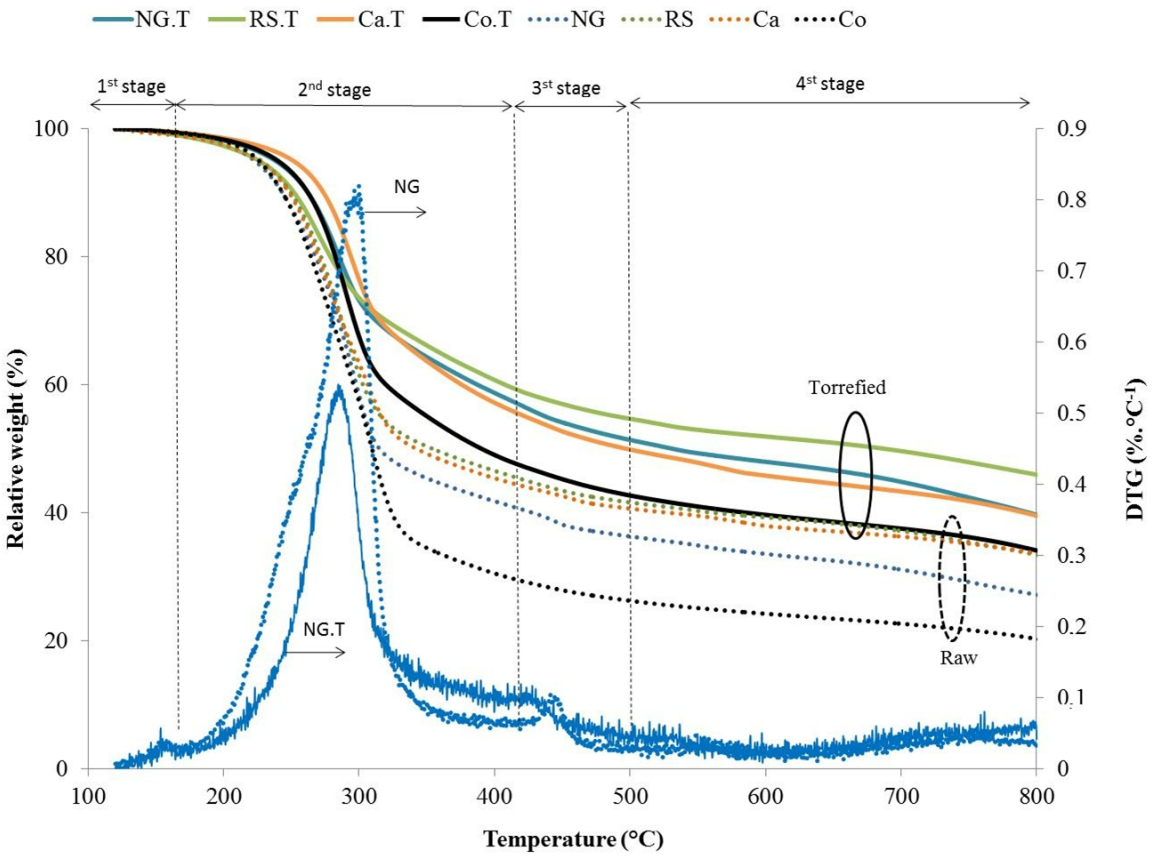

Figure 4: TGA at 800°C under nitrogen for raw and correspondent torrefied biomass. DTG for raw (NG) and torrefied NG (NG.T). T= torrefied. NG=Napier grass; RS = Rice straw; Ca = Cassava stalks; Co = Corn cob

Since the interactive effects varied with the characteristics of the components in the blends, e.g. heterogeneity, nature and distribution of reacting species, etc., synergies during the pyrolysis process were difficult to predict. To evaluate the interactions between the raw biomasses studied, the experimental and calculated TGA curves were plotted as shown in **Figure 5.** The predicted results were obtained from the calculations in terms of weight percentage of every single material. It can be seen that for the raw blends, whichever the ratios, all the calculated curves were found to almost overlap with the experimental ones. This entails that the pyrolytic characteristics of the blends followed those of the parent fuels in an additive manner. The fuels did not chemically interact when blended under inert condition. This confirms the hypothesis made by a number of researchers about the general lack of synergistic effects in the yield of pyrolysis products from blended agriculture residues (Meesri *et al.* 2002, Moghtaderi *et al.* 2004). These results reveal that the pyrolysis behaviour of the mixture can be predicted through linear superposition in terms of the weight percentage of every single material.

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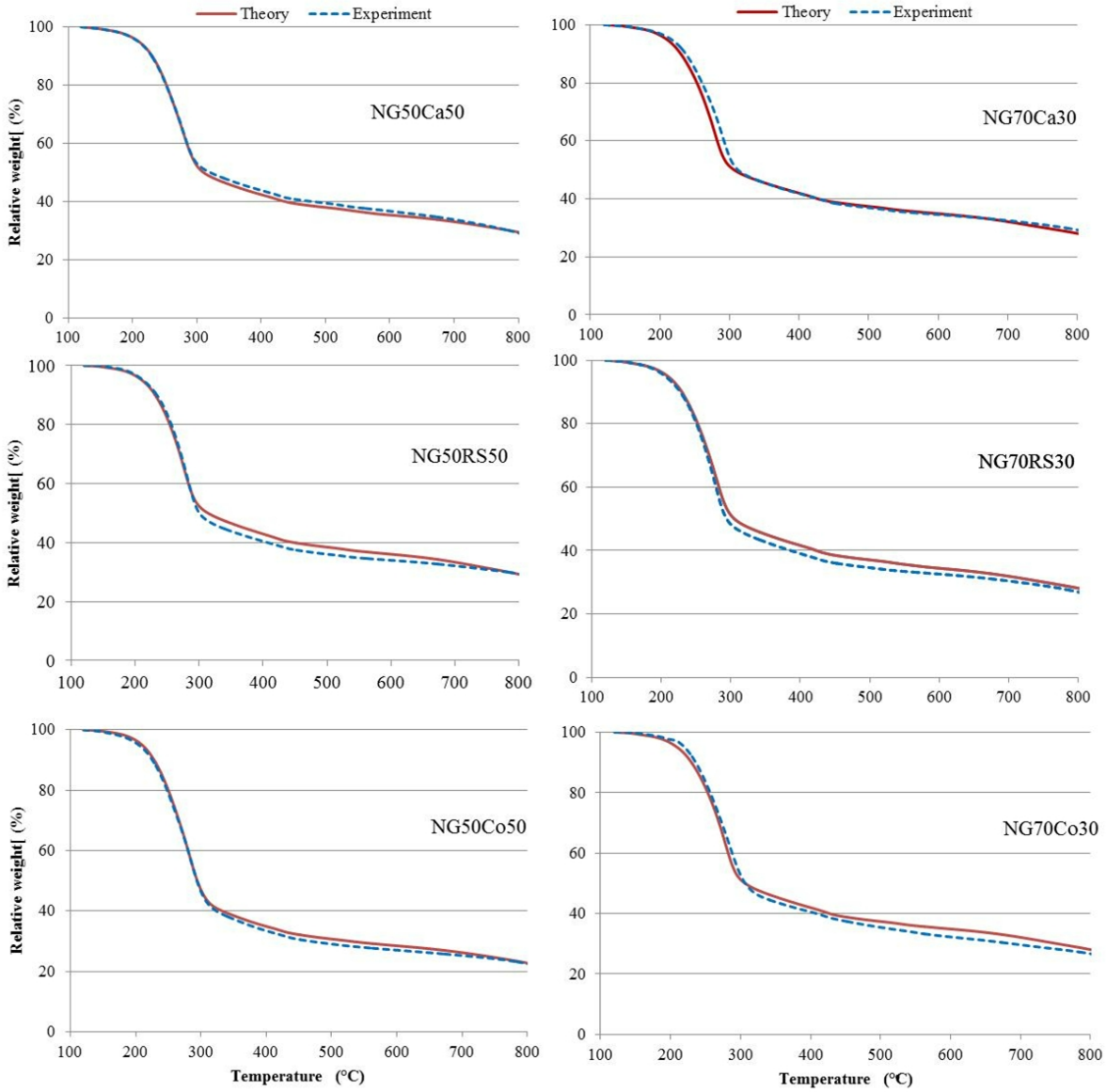

Figure 5: Comparisons of experimental and calculated TGA curves of raw napier grass (NG) and Cassava stalks (Ca), Rice straw (RS) and Corn cob (Co) blend at 50:50 and 70:30 ratios.

Figure 6 presents experimental and calculated TGA and DTG curves under nitrogen for NG mixed before (BT) or after (AT) torrefaction with RS and Ca successively at the ratios of 50:50 and 70:30. The objective is to demonstrate if blending biomass before or after torrefaction affects pyrolytic characteristics. Each experiment was repeated three times to obtain adequate average figures. The four torrefied biomasses were the parent fuels for all theoretical curves. For all blends and whichever the ratios, BT and AT's TGA curves showed significant differences in terms of pyrolysis behaviour. At 800°C, the solid residues were found to be 53, 39, 48 and 38% for NA50RS50 (BT), NA50RS50 (AT), NA50Ca50 (BT), and NA50Ca50 (AT) respectively. With the ratio 70:30, solid residues were found to be lower (48 and 43%) for NG blended with RS than for NG blended with Ca (53 and 40%). According to the distributions of the DTG curves, the decomposition intensity ranged from 0.49 to 0.56 wt. %. $°C^{-1}$, with a maximum reached for NA70RS30.

In co-pyrolysis, significant synergetic effects were observed for biomasses mixed before torrefaction (BT). After torrefaction (AT), a slight synergistic effect was observed for the 50:50 ratio only. The experimental curves showed the blends (BT) to be more reactive than based on the calculated curves. This synergetic effect could be explained by the catalytic role played by alkali metal salts (Brown *et*

al. 2000), especially those containing potassium as shown in **Error! Reference source not found.Table 2**. Previous studies have indicated that cellulose can show positive synergistic effects on the thermal decomposition of blending biomass. hemicellulose and lignin showed both positive or negative synergistic effect in this temperature range (Wu *et al.* 2014). More investigations are necessary to evaluate how inorganics may affect the pyrolytic behaviour of biomass blends. The results obtained from this comprehensive investigation indicates that the pyrolytic characteristics of mixtures can be different depending on whether the biomasses were blended before or after torrefaction.

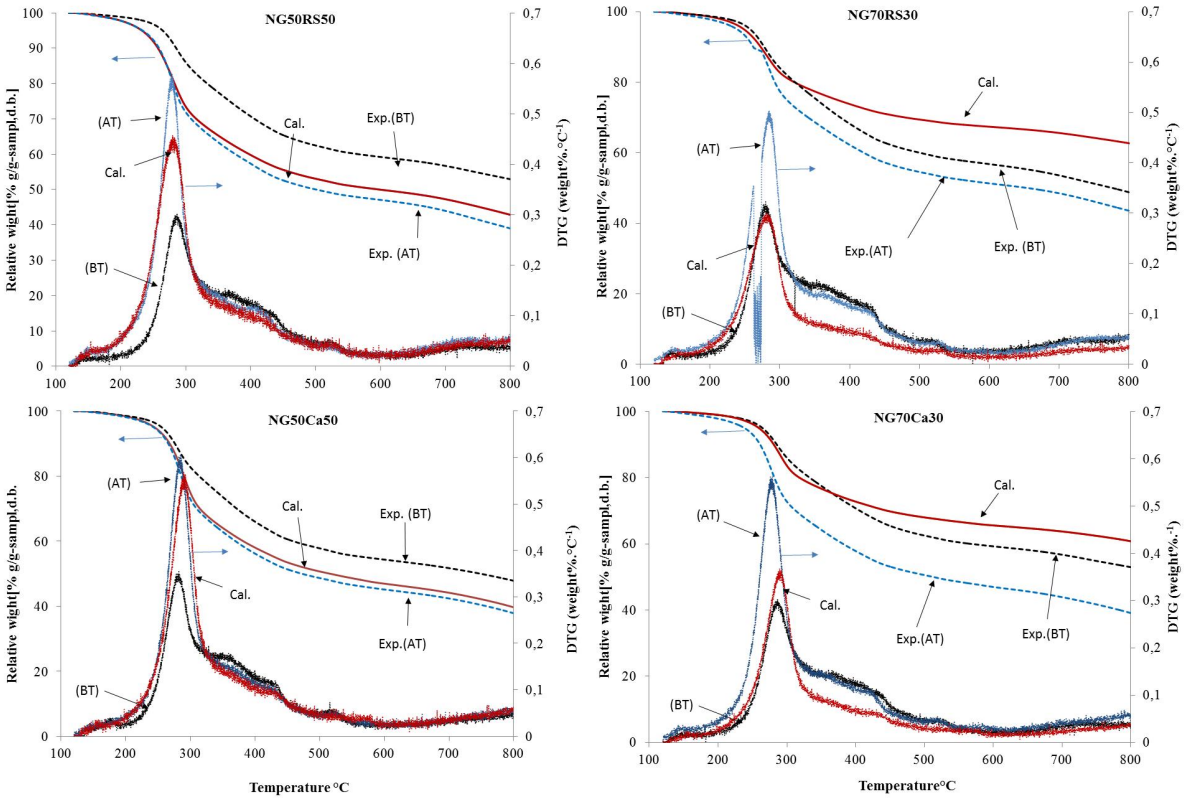

Figure 6: Comparisons of experimental and calculated TGA and DTG curves of torrefied napier grass (NG) blended at 50:50 and 70:30 with torrefied Rice straw (RS) and Cassava (Ca) 50:50 and 70:30 ratios. (BT) = before torrefaction; (AT) = after torrefaction; Cal. = Calculation.

3.4. Ignition and burnout temperature

The ignition temperature is a crucial index to stand for the ignitability and reactivity of fuels, including raw and torrefied biomasses. In the industry, the higher the ignition temperature, the safer the fuel's storage and delivery (Chen *et al.* 2016). **Table 4** shows the ignition temperatures of 11 different biofuels before and after torrefaction where the temperatures were obtained based on the intersection method (Lu and Chen 2015). Overall, the ignition temperatures of the raw biomasses were found to lie between 235 °C and 260 °C which are generally lower than those of coals (>300 °C) (Du, Wang et al. 2014). The maximum was found for NG (248°C) and the mix with Ca (260°C) in 70:30 ratio. Co was found the more instable with an ignition temperature below 240°C. The ignition of raw biomass triggered is mainly due to the thermal decomposition of hemicellulose and cellulose where volatiles are released and ignited. After the biomass materials undergo torrefaction, the table indicates that the ignition temperatures are raised to around 250-288 °C meaning torrefied biomasses were less reactive than untreated biomasses. This is due to the devolatilization and depolymerization process in the course of torrefaction (Rousset *et al.* 2012) so that less volatile are retained in the biomass. The table

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also suggests that the ignition temperature can be raised up to 51 °C for Co, showing the significant impact of torrefaction upon the reactivity of biomass.

The burnout temperature, calculated via the conversion method (Lu and Chen 2015) with 110 and 800 °C as the initial and final states, represents the temperature at which the fuel is almost completely consumed and therefore provides a useful insight into the operation of biomass combustion and design of reactor or combustor. The results show that the burnout temperatures of the raw biomasses ranged from 773 °C to 787 °C, implying that over 99% of the biomasses were consumed when the temperature exceeded 787 °C. Alternatively, burnout temperatures of the torrefied biomass samples were found to be in the range 786-795 °C. Significant differences were observed for blends with same biomasses but different ratios. The higher the ratio, the lower the difference ΔT. Similarly, by virtue of devolatilization from torrefaction, relatively less volatiles and more carbonaceous matters are contained in torrefied biomass. This explains the higher burnout temperatures obtained for the torrefied biomasses compared to their respective parent biomasses.

Table 4: Combustion characteristic s of raw and blended biomasses. Ti : ignition temperature - Tb : burnout temperature - * : $T_{Tor} - T_{Raw}$. NG=Napier grass; RS = Rice straw; Ca = Cassava stalks; Co = Corn cob

Material	Ti (°C)			Tb (°C)		
	Raw	Tor	Δ T*	Raw	Tor	Δ T*
NG	248.22	269.93	21.71	781.44	788.31	6.87
RS	245.04	250.67	5.63	783.62	786.15	2.53
Ca	246.09	284.31	38.22	773.00	786.24	13.24
Co	236.53	287.76	51.23	780.59	794.48	13.89
NG50RS50	245.74	274.02	28.28	773.85	787.64	13.79
NG70RS30	248.13	259.99	11.86	786.88	789.67	2.79
NG50Ca50	242.91	263.37	20.46	785.44	794.95	9.51
NG70Ca30	260.43	265.42	4.99	780.16	787.36	7.20
NG50Co50	246.84	258.01	11.17	772.77	787.57	14.80
NG70Co30	255.45	265.29	9.84	774.94	787.35	12.41

This comprehensive study indicates that blending different biomass species undergoing torrefaction treatment may be an option to produce a uniform feedstock for biofuel production with more energy and less chlorine content avoiding fouling during combustion. Expanding knowledge on these biomass traits will play a critical role in enhancing the utilization of agricultural waste for energy, particularly in agriculture based-country.

4. Conclusion

This study investigated the pyrolytic behaviour and quantified the chlorine release of blended agriculture residues and their parents exposed to a high torrefaction temperature (300°C) performed in a thermogravimetric balance (microparticle) and a batch reactor (macroparticle).
The FC:VM fuel ratio indicated that torrefaction was more efficient for rice straw. If we consider the lowest ash content and the highest HHV separately as indicators for combustion, the best blends were found to be for the 50:50 ratios between napier grass, corn cob and rice straw.
The greatest chlorine content mitigation was observed for the mix of napier grass and rice straw with 56% decrease. The HHV: Cl ratio, an indicator of combustion quality, showed that napier grass mixed with rice straw in 50:50 proportion was the most promising blend with the highest ratio (6.3).
According to the distributions of TGA curves, two groups composed by raw and torrefied biomasses were distinctly observable. Torrefied biomasses were found less reactive than the control. The pyrolytic characteristics of the blends followed those of the parent fuels in an additive manner.

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Blending biomasses before or after torrefaction affected pyrolytic characteristics differently. In the case of co-pyrolysis, a significant synergetic effect was observed for biomasses mixed before torrefaction, while after torrefaction a slight synergistic effect was observed for 50:50 ratios only and mainly due to the catalytic role of alkali metal salts.

The K_2O:SiO_2 which is the fouling risk index determining if biofuel require special precautions to avoid fouling problems, was lower for torrefied biomasses compared to untreated blends.

The ignition temperatures of the raw biomasses and their blends were found to lie between 235 °C and 260 °C while torrefied materials showed ignition temperatures in the range 250-288 °C. Torrefied individual and blended biomasses presented in all cases higher burnout temperatures than the untreated biomasses.

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